PYROELECTRIC PROPERTIES OF LEAD ZIRCONIUM TITANATE ($PbZr_{0.525}Ti_{0.475}O_3$) METAL FERROELECTRIC-METAL CAPACITOR AND ITS APPLICATION FOR IR SENSOR

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ABSTRACT

PYROELECTRIC PROPERTIES OF LEAD ZIRCONIUM TITANATE ($PbZr_{0.525}Ti_{0.475}O_3$) METAL-FERROELECTRIC-METAL CAPACITOR AND ITS APPLICATION FOR IR SENSOR. Thin films lead zirconium titanate ($PbZr_{0.525}Ti_{0.475}O_3$) prepared on Pt(200)/$SiO_2$/Si(100) substrates using chemical solution deposition (CSD) method for 0.5 M solution have been investigated. The films were grown by spin coating at 2500, 3000, 3500 rpm for 30 seconds, and then annealing at 750^{o}C for 3 hours. X-ray diffraction (XRD), pyroelectric properties observation were employed to characterize the grown films. The film shows tetragonal structure with lattice constants are a = b = 4.141 Å, c = 3.828 Å. The voltage responsivity (r_v) measured at chopper frequency of 2000 Hz and at wavelength of 947 nm are between 32.7-44.9 μV/W. Meanwhile, the pyroelectric coefficient (*p*) are in the range of 5.01 x 10^{-4}-6.88 x 10^{-4} C/m^{2}K for PZT thin films. These results show that PZT thin films are suitable for use as a pyroelectric IR sensor.

Key words : $PbZr_{0.525}Ti_{0.475}O_3$ thin films, CSD method, metal-ferroelectric-metal capacitor, pyroelectric coefficient, IR sensor

ABSTRAK

SIFAT PIROELEKTRIK KAPASITOR LOGAM-FEROELEKTRIK-LOGAM TIMBAL ZIRKONIUM TITANAT ($PbZr_{0,525}Ti_{0,475}O_3$) DAN APLIKASINYA UNTUK SENSOR IR. Telah diteliti lapisan tipis timbal zirconium titanat ($PbZr_{0,525}Ti_{0,475}O_3$) telah disiapkan pada substrat Pt(200)/SiO_2/Si(100) dengan menggunakan metode deposisi larutan kimia (CSD) untuk larutan 0,5 M. Film ini ditumbuhkan dengan *spin coating* pada kecepatan putar 2500 rpm, 3000 rpm, 3500 rpm selama 30 detik, dan *anneal* pada 750^{o}C selama 3 jam. Pengamatan difraksi sinar-x (XRD), sifat-sifat piroelektrik dilakukan untuk melihat sifat-sifat film. Lapisan tipis ini menunjukkan struktur tetragonal dengan parameter kisi *a* = *b* = 4,141 Å, *c* = 3,828 Å. Responsivitas tegangan (r_v) yang diukur pada frekuensi pemotong 2000 Hz dan panjang gelombang 947 nm adalah antara 32,7 μV/W sampai dengan 44,9 μV/W. Sementara itu, koefisien piroelektrik (*p*) dalam jangkauan 5,01 x 10^{-4} C/m^{2}K sampai dengan 6,88 x 10^{-4} C/m^{2}K untuk lapisan tipis PZT. Hasil-hasil ini menunjukkan bahwa lapisan tipis PZT sangat memadai sebagai sensor IR piroelektrik.

Kata kunci : Lapisan tipis $PbZr_{0,525}Ti_{0,475}O_3$, metode CSD, kapasitor logam-feroelektrik-logam, koefisien piroelektrik, sensor IR

INTRODUCTION

A pyroelectric infrared (IR) detector has advantages of wavelight independent sensitivity and can be operated at room temperature. It is also expected to provide various thermal observations for objects at near ambient temperature. Thin films of $PbTiO_3$ and $PbZr_xTi_{1-x}O_3$ have been used as pyroelectric IR detectors [1]. Merit of $PbTiO_3$ and $PbZr_xTi_{1-x}O_3$ based pyrosensor compared to other infrared sensor materials, such as semiconductors are: wide range of response frequency, use at room temperature, quick response in comparison with other temperature sensors and high quality materials for the pyrosensor is unnecessary [2].

$PbZr_xTi_{1-x}O_3$ films can be grown by various methods, such as sputtering [2-8], chemical solution

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Table 1. CSD deposition parameter

Film	$PbZr_{0.525}Ti_{0.475}O_3$
Substrate	Pt(200)/SiO_2/Si(100)
Pt (200) substrate thickness	150 nm
Solution	0.5 M $PbZr_{0.525}Ti_{0.475}O_3$ in precursor 2-methoxyethanol
Deposition angular frequency	2500 rpm, 3000 rpm, 3500 rpm for 30 seconds
Annealing temperature	750°C for 3 hour
Contact Au thickness	100 nm

Table 2. Growth condition of PZT thin films using CSD method

Substrates	Treatment	Angular frequency (rpm)	Deposition Duration (second)	Annealing Temperature (°C)	Annealing duration (hour)
Pt/(200)/ SiO_2/Si(100)	I	2500	30	750	3
	II	3000			
	III	3500			

deposition (CSD) [9-13], pulsed laser deposition (PLD) [14,15], and metal organic chemical vapor deposition (MOCVD) [16]. The varian of chemical solution deposition (CSD) method, which is, the CSD method is of particular interest because of its good control of stoichiometry, ease of fabrication and low or high temperature synthesis. It was reported that CSD derived is thermodynamically stable.

Lead zirconium titanate (PZT) has been of immense interest in the use of ferroelectric thin film in pyroelectric sensor applications [2]. The pyroelectric properties of the materials can be tailored by varying the angular frequency. Since the sensor performance significantly depend on these properties, the sensor performance can then be optimized.

In this paper we report the fabrication of lead zirconium titanate [$PbZr_{0.525}Ti_{0.475}O_3$] thin films by CSD method. The crystal structure, and the pyroelectric properties of the grown films related to the angular frequency are described.

METHOD

PZT thin film was fabricated by CSD methods using 0.83 gram PZT as a precursor in 5 mL 2-methoxyethanol [$H_3COCH_2CH_2OH$, 99.9 %] which was used as solvent and then using ultrasonic Model Branson 2210 for 1 hour to get the clear liquid. After 20 minutes of left at room temperature, this solution shows a milky appearance, that it contains an equivalent 0.5 M PZT. After 2 hours of aging, that solution described above was applied on 12 mm x 12 mm Pt (200)/Si (100) substrate, then prepared by spin coating at 2500, 3000 and 3500 rpm for 30 seconds. The deposition parameter are shown in Table 1. The growth condition of PZT thin films using CSD method are given in Table 2.

The post deposition annealing of the films was carried out in a Furnace Model Nabertherm Type 27 at 750°C for 3 hours in an air atmosphere. The structure of the grown films was analyzed by x-ray diffraction (XRD). The XRD spectra were recorded on a Diano type 2100E

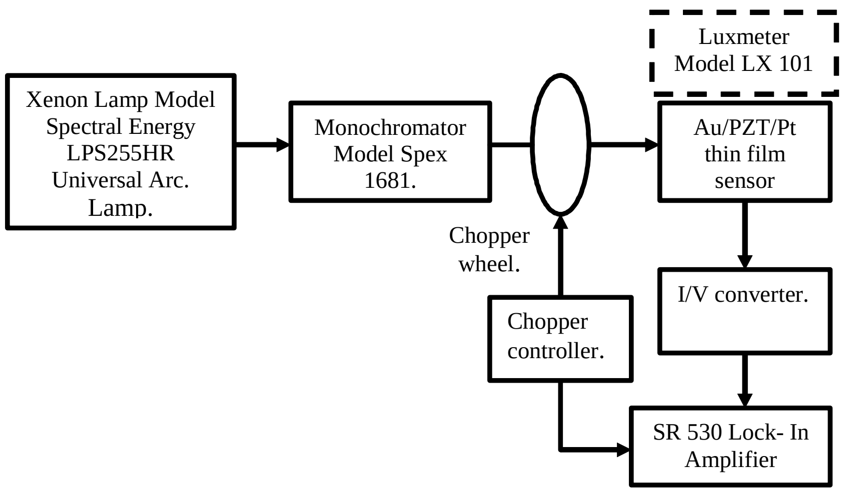

Figure 1. A Schematic diagram of the voltage responsivity and the pyroelectric coefficient measurements [17,18,19]

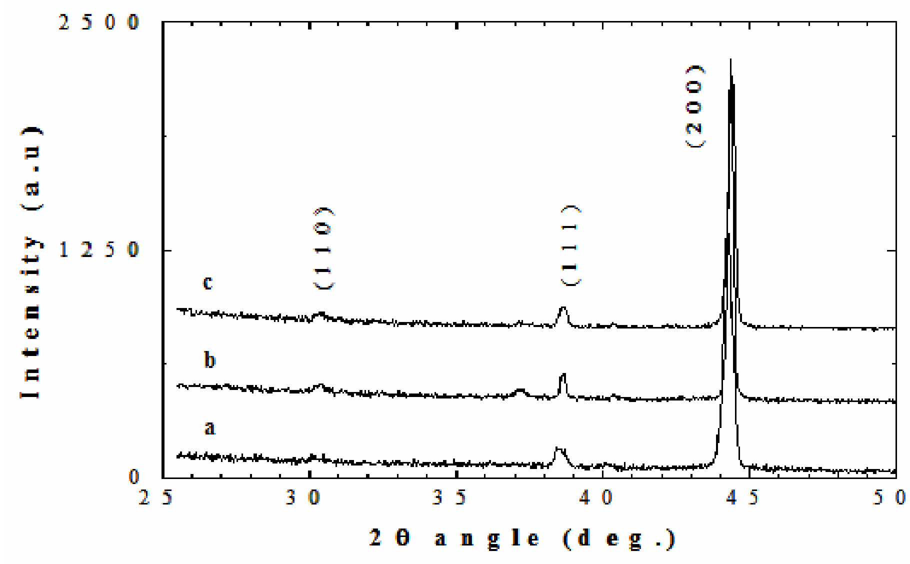

Figure 2. A XRD spectra of $PbZr_{0.525}Ti_{0.475}O_3$ (PZT) on Pt(200)/SiO_2/Si(100) substrate at various angular frequency. (a) 2500 rpm (b) 3000 rpm (c)3500 rpm

diffractometer using CuK_α radiation at 30 KV and 30 mA. The voltage responsivity and the pyroelectric coefficient were examined by means of I-V measurement on a capacitor structure of Au/PZT/Pt and Au/PTZT/Pt using the lock-in technique. The capacitor was fabricated by making Au contacts on top of the grown film. The size of the contact was about 1.0 mm^2 and fabricated by thermal evaporation. The flow diagram of this experimental procedure is give at Figure 1.

Figure 1 shows a schematic diagram of the voltage responsivity and the pyroelectric coefficient measurements [17,18,19]. The visible and infrared source was a Xenon lamp model Spectral Energy LPS255HR Universal Arc Lamp. The Spex 1681 Monochromator was used to provide monochromatic wavelength at 600 - 1000 nm. The variation in electric charge or current density in the capacitor Au/PZT/Pt and Au/PTZT/Pt were then converted to voltage using I/V converter. Finally, SR 530 Lock- in Amplifier was used to extract the voltage. The voltage responsivity (r_v) is charge generation associated with the change of spontaneous polarization due to pyroelectric effect and is given by equation (1) [2, 17, 18, 19, 24]:

$$\boldsymbol{r_v} = \frac{\boldsymbol{V_o}}{\boldsymbol{P_i}} = \frac{\boldsymbol{\eta p}}{(\boldsymbol{\rho c_p \varepsilon \varepsilon_0 A \omega})}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where: V_o = output voltage
P_i = input power of incident radiation
η = the transmittance of incident radiation
ρ = mass density
c_p = the specific heat
ε = relative permitivity
ε_0 = permitivity of vacuum
A = a contact area
ω = angular chopper modulation frequency

RESULTS AND DISCUSSION

X-ray diffraction (XRD) measurements was used to determine the crystallinity of PZT ceramic and thin film. From the XRD result, PZT ceramic are polycrystalline with tetragonal structure. The lattice constants are a = b = 4.094 Å, c = 4.142 Å, c/a ratio = 1.012 These values are in good agreement with those observed by other researchers [25].

Figure 2 shows XRD spectra of $PbZr_{0.525}Ti_{0.475}O_3$ thin film with a tetragonal phase. The diffraction peaks (110), (111), (200) crystal planes of tetragonal PZT thin films on Pt(200)/SiO_2/ Si(100) substrates were used for calculating lattice constants a, b, and c. The XRD spectra shows that PZT films is a tetragonal structure with the calculated lattice constants are a = b = 4.141 Å, and c = 3.828 Å.

Figure 3 shows the voltage responsivity (r_v) as function of angular frequency. The voltage responsivity (r_v) at λ = 947 nm are between 32.7-44.9 μV/W for PZT thin films. These values are

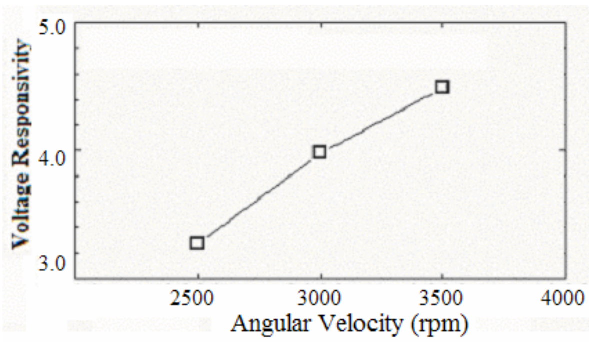

Figure 3. The voltage responsivity (r_v) at λ = 947 nm of Au/PZT/Pt as a function of Angular frequency, V_{bias} = 5 volt and chopper frequency = 2000 Hz

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better than those of $LiTaO_3$ and PZT, which are 3200 μV/W [26] and 62,1-80 μV/W [17].

The pyroelectric coefficient (p) were calculated from the voltage responsivity (r_v) using parameter listed in Table 3. Figure 4 shows the pyroelectric coefficient PZT thin films as a function angular frequency. The pyroelectric coefficients increase as the angular frequency are increased.

Table 3. Parameter for calculation of the pyroelectric coefficient of PZT thin films

Parameter	Value
Dielectric constant (ε) of PZT and PTZT	57.44 [a]
Mass density (ρ) of PZT and PTZT	7,500 kg/m^3 [b]
Specific heat (c_p) of PZT and PTZT	3.2 x 10^6 J/(m^{3}K) [c]
Relative permitivity of vacuum (ε_0)	8.854 x 10^{-12} C^2/(Nm^2)
Contact area (A)	1 x 10^{-6} m^2
Transmittance of incident radiation (η)	0.005 [d]
Angular chopper modulation frequency (ω)	6280 rad/s

[a] Ref. [17], [b] Ref. [27], [c] Ref. [28], [d] Ref. [29].

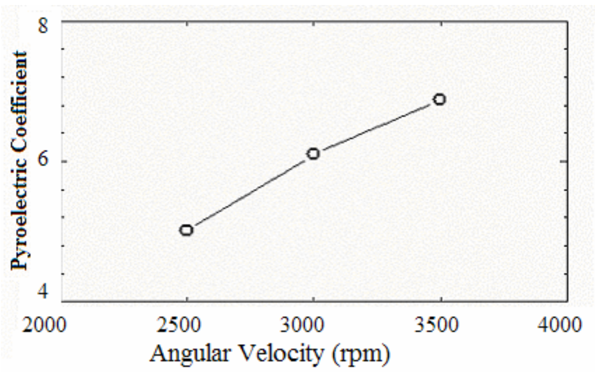

Figure 4. The pyroelectric coefficient (p) at λ= 947 nm of Au/PZT/Pt and as a function of angular frequency, V_{bias} = 5 volt and chopper frequency = 2000 Hz

In general, the calculated pyroelectric coefficients are better than those of TGS single crystal, $LiTaO_3$ single crystal, $BaTiO_3$ ceramic, PZT ceramic, $PbTiO_3$ polycrystal which are 3.5 x 10^{-4} C/(m^{2}K), 2.0 x 10^{-4} C/(m^{2}K), 4.0 x 10^{-4} C/(m^{2}K), 4.2 x 10^{-4} C/(m^{2}K), 2.3 x 10^{-4} C/(m^{2}K) respectively [30], or PLZT (6/80/20) ceramic, PVDF polymers thin film which are 7.6 x 10^{-4} C/(m^{2}K), 0.3 x 10^{-4} C/(m^{2}K) [30] or PZT thin film, PTZT (1/52.5/47.5) thin film which are 12.3 x 10^{-4} C/(m^{2}K), 11.7 x 10^{-4} C/(m^{2}K) [17].

The pyroelectric sensor is a device for transducing optical/thermal energy to electrical energy. Its figure of merit is evaluated in several ways includes : low impedance amplifier (p/c_p), high impedance amplifier ($p/[c_p\varepsilon\ \varepsilon_0]$) and high impedance amplifier when the pyroelectric element is the main noise source $\{p/[c_p(\varepsilon_0\ tan\ \delta)^{1/2}]\}$[2,17,30]. Table 4 compare figure of merit of several pyroelectric materials, including our result. Figure of merits of PZT thin film are higher than those of TGS thin film, $LiTaO_3$ thin film, PVDF thin film, and $Sr_{0.5}Ba_{0.5}Nb_2O_6$ ceramic as shown in Table 4. This is because of high pyroelectric coefficient and small dielectric constants of PZT thin films. The results show that PZT thin films were suitable for use as a pyroelectric IR sensor

CONCLUSIONS

We have investigated the dependence of angular frequency on pyroelectric properties of PZT thin films grown by the CSD method. The $PbZr_{0.525}Ti_{0.475}O_3$ (PZT) ceramic by solid solution method and the PZT thin film by the chemical solution deposition (CSD) method. The ceramics are polycrystalline in tetragonal structure, the the thin films are also polycrystalline in tetragonal structure. The crystalline quality of the grown film significantly depends on the angular frequency. Compared to other pyroelectric materials, PZT thin

Table 4. Room temperature properties of various pyroelectric detector materials and some figure of merit for their detector operation

Material	p (C/(m^{2}K)	$\varepsilon/\varepsilon_0$	c_p (J/(m^{3}K))	p/c_p (Am/W)	$p/(c_p\varepsilon\ \varepsilon_0)$ (V/(m^{2}J))	$p/(c_p[tan\delta\ \varepsilon_0]^{1/2})$ (m^3/J)$^{1/2}$
TGS thin film [a]	3.0 x 10^{-4}	50	1.70 x10^6	1.78 x 10^{-10}	0.400	1.49 x10^{-4}
$LiTaO_3$ thin film [a]	1.9 x 10^{-4}	46	3.19 x10^6	0.60 x 10^{-10}	0.147	0.50 x10^{-4}
$Sr_{0.5}Ba_{0.5}Nb_2O_6$ ceramic [a]	6.0 x 10^{-4}	400	2.34 x10^6	2.56 x 10^{-10}	0.072	0.30 x10^{-4}
PLZT (6/80/20) ceramic [a]	7.6 x 10^{-4}	1,000	2.57 x10^6	2.99 x 10^{-10}	0.034	0.34 x10^{-4}
PVDF thin film [a]	0.3 x 10^{-4}	11	2.4 x10^6	0.13 x 10^{-10}	0.129	0.09 x10^{-4}
PZT thin film using DC UBMS method [b]	12.3 x 10^{-4}	57.44 [b]	3.2 x10^6 [d]	3.84 x 10^{-10}	0.756	1.71 x10^{-4}
PTZT thin film using DC UBMS method (1/52.5/47.5) [b]	11.7 x 10^{-4}	57.44 [b]	3.2 x10^6 [d]	3.66 x 10^{-10}	0.719	1.63 x10^{-4}
PZT thin film using CSD method [c]	6.88 x 10^{-4}	57.44 [b]	3.2 x10^6 [d]	2.15 x 10^{-10}	0.423	0.96 x10^{-4}

[a] Ref. [2, 30], [b], Ref. [17], [c] our experimental, [d] Ref. [28].

films have good figure of merits and are suitable for use as a pyroelectric IR sensor.

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REFERENCES

[1]. T. WHITAKER, *Compound Semiconductor Spring II*, **4** (4), (1998) 17

[2]. K. UCHINO, *Ferroelectric Devices*, Marcel Dekker, Inc. New York, (2000) 23

[3]. N.J. WU, Y.S. CHEN, S. DORDERIC, and A. IGNATIEV, *Proceeding Third International Conference on Thin Film Physiscs and Applications*. SPIE 3175, (1997) 256

[4]. K. SUU, *Jpn. J. Appl. Phys*., **35** (9B), (1996) 4967

[5]. IRZAMAN, A. FUAD dan M. BARMAWI, *Prosiding Pertemuan Ilmiah Ilmu Pengetahuan dan Teknologi Bahan'99*, Serpong, (1999) 196

[6]. N.A.K. UMIATI, IRZAMAN, M. BUDIMAN, M. BARMAWI, *Jurnal Kontribusi Fisika Indonesia*. ITB Bandung, **12** (4), (2001) 94

[7]. C. LATIEF, *Dissertation Institut Teknologi Bandung* (ITB), Bandung, (1997) 10

[8]. N. SAVVIDES and A. KATSAROS, *Appl. Phys. Lett*., **62** (5), (1993) 528

[9]. L. PINTILIE, M. ALEXE, I. PINTILIE and T. BOTILA,. *Appl. Phys. Lett*., **69** (11), (1996) 1571

[10]. Y. HIDEKAZE, *Jpn. J. Appl. Phys*., **35** (9B) (1996) 4941

[11]. J.Y. ZHANG, and I.W. BOYD, *Jpn. J. Appl. Phys*., **38** (4A), (1999) L393

[12]. Y. FUJIMORI, T. NAKAMURA and H. TAKASU, *Jpn. J. Appl. Phys*., **38** (9B), (1999) 5346

[13]. C.R. CHO, W.J. LEE, B.G. YU and B.W. KIM, *J. Appl. Phys*., **86** (5), (1999) 2700

[14]. D.J. DI MARIA,. *J. Appl. Phys*., **86** (3), (1999) 1630

[15]. H. WU., J. YU, X. DONG, W. ZHOU and Y. WANG, *Jpn. J. Appl. Phys*., **40** (3A), (2001) 1388

[16] J.H. KIM, and F.F. LANGE, *J. Mater. Res*., **14** (10), (1999) 4004

[17]. IRZAMAN, Y. DARVINA, A. FUAD, P. ARIFIN, M. BUDIMAN, M. BARMAWI, *Journal of Physica Status Solidi (a)*, **199** (3), (2003) 416

[18]. Y. CHEN, H.L.W. CHAN, N.M. HUI, Y.W. WONG and C.L. CHOY, *Sensor and Actuator*, **A** (69), (1998) 156

[19]. D. SETIADI, *Thesis Universiteit Twente*, Cip Data Koninklijke Bibliotheek, Den Haag, (1995) 111

[20]. B.D. CULLITY, *Elements of X-ray Diffraction*, Second Edition, Addison Wesley Publishing Company Inc., London, (1978) 366

[21]. C. SURYANARAYANA and M.G. NORTON, X-*ray Diffraction : A Practical Approach,* Plenum Press, London, (1998) 125

[22]. M.R. SPIEGEL, *Advanced Mathematics for Engineers and Scientific*, McGraw-Hill International Book Company, New York, (1983)

[23]. G.B. ARFKEN and H.J. WEBER, *Mathematical Methods for Physicists*, Fourth Edition, Academic Press, Inc, San Diego, (1995) 156

[24]. IRZAMAN, A. FUAD, P. ARIFIN, M. BUDIMAN and M. BARMAWI, *Submitted to Journal of Physica Status Solidi (a)*, Germany, (2003)

[25]. KAKEGAWA, (1977) : in JCPDS-International Center for Diffraction Data (JCPDS-ICDD), (1995)

[26]. I.R. SINCLAIR, *Sensor and Transducers A Guide for Technology*. Newnes, Great Britain, Second Edition, (1992) 96

[27]. J. FRADEN, *Handbook of Modern Sensors : Physics, Designs and Applications*, Springer-Verlag Berlin, Second Edition, (1996) 536

[28]. J.J. HO, Y.K. FANG, W.J. LEE, F.Y. CHEN, W.T. HSIEH, S.F. TING, M.S. JU, S.B. HUANG, K.H. WU and C.Y. CHEN, *IEEE Transaction on Electron Devices*, **46** (12), (1999) 2289

[29]. E. UIGA, *Optoelectronics*, Prentice-Hall of India Private Limited, New Delhi, (1995) 55

[30]. M.E. LINES and A.M. GLASS, *Principles and Applications of Ferroelectric and Related Materials*, Claredon Press, Oxford, (1977) 570